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(54) Title: PLASTICIZER-ASSISTED BOND FORMATION USEFUL FOR DEFECT-FREE LAMINATION

(57) Abstract

Laminated articles of the present invention are prepared using at least substrate to be bonded, a polymeric film, and a non-volatile plasticizer for coating at least one surface of the substrate or polymeric film to be bonded. Upon absorption of the plasticizer into the polymeric film, a laminate article is formed. Preferred laminates are useful in optical applications and do not require elevated temperatures and non-atmospheric pressures for timely bonding. Kits comprising an amorphous polymeric film and a sufficient amount of a non-volatile plasticizer for forming a laminate comprising the amorphous polymeric film and a substrate are also useful for practicing the method of the invention.

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**PLASTICIZER-ASSISTED BOND FORMATION USEFUL FOR  
DEFECT-FREE LAMINATION**

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**Field of the Invention**

This invention pertains to plasticizer-assisted bond formation useful for defect-free lamination.

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**Background of the Invention**

Laminated articles are used in a multitude of applications. As would be expected, numerous lamination methods have been used to prepare laminated articles. While the objective of many lamination methods is solely the joining of two substrates, certain applications have additional requirements to achieve the full utility of the laminate article.

15

For example, glass laminates may be used in optical applications where it is necessary or desirable to see through the laminate, preferably with an undistorted view. Typically two substrates are bonded together with a material therebetween. One such application is glass laminates used for safety glass, such as that used in automobiles, where a layer of, for example, polyvinyl butyral, can be laminated between two glass sheets.

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It may also be desirable to bond two substrates together, such as when each substrate comprises a different material. One of the substrates may be comparatively rigid, while the other substrate may be comparatively flexible. For example, a solar control film, such as those described in U.S. Patent No. 3,681,179 (Theissen), may be laminated to a glass substrate. Films described therein include pressure-sensitive adhesive acrylate copolymers overcoated with a dried coating of a water-soluble overcoat, which overcoat may include up to about 15% water-soluble plasticizers. It is preferred that the water-soluble overcoat is incompatible with pressure sensitive adhesives comprising the film so as to prevent any gradual plasticization of the pressure sensitive adhesive. The solar control films are wet with water to bond them to a substrate. It is taught that after drying for approximately two hours, edges of the product are firmly bonded, but it took about three days for the entire product to develop a firm adhesion to windows.

Furthermore, polymeric films useful for repairing glass substrates may also be bonded to form laminates, such as described in copending U.S. Patent Application Serial No. 09/181,198, assigned to the assignee of the present application and entitled "Repaired Scratched and/or Abraded Transparent Substrates Having Protective Removable Sheets Thereon and a Method of Making." Preferred films include poly(meth)acrylates, polyolefins, silicones, or rubber-based pressure sensitive adhesives that have a stress relaxation value of about 15 percent or greater. These polymeric films are typically wet with water or solutions of water and detergent and then bonded to the glass substrate.

As described, the above methods and other conventional methods utilize water to wet surfaces to be bonded in order for a bond to develop between the surfaces. However, the use of water has its drawbacks. For example, as water is volatile at typical bonding temperatures, it evaporates from the laminate assembly during the drying step necessary to complete bond formation. That is, water is essentially not present in the ultimate dried laminate assembly. For the final bond to form, water must, therefore, escape from the laminate assembly. Depending on the materials and construction of the laminate assembly, bond formation may take several hours or days to complete. While this may be satisfactory for certain applications (e.g., those where repositioning of the surfaces to be bonded needs to occur after activating the bonding mechanism), more timely bonding may be desirable or necessary for certain applications. Furthermore, until the laminate assembly is completely dry, the laminate assembly may appear hazy. For optical applications, the haziness may be problematic, especially if it lasts for several days.

Particularly problematic with laminating glass is the persistent entrapment of air between the layers during lamination. Residual air bubbles remain as "defects" in the final laminate. The defects may impair ones ability to see through the laminate.

Many conventional methods of laminating glass involve laminating a plastic material between two sheets of glass. For example, see Nichols, R.T. and R.M. Sowers, "Laminated Materials, Glass," Kirk-Othmer Encyclopedia of Chemical Technology, 4<sup>th</sup> Ed., where methods of laminating glass are described. In one conventional lamination method, the glass sheets are assembled with a plastic material sandwiched therebetween, after which the sandwich construction is passed between heated pinch rolls at about 40 psi to exclude air from between the sheets and to obtain an initial bond. The laminated sheet is then placed in an autoclave to remove further air. In the autoclave, the sheet is further

heated to about 275°F at about 30 psi pressure for about 20 to 30 minutes. There are drawbacks to this method however. For example, the equipment required to make laminated glass in this manner is large and expensive. Furthermore, the number of steps involved in the process hinders the efficiency of this lamination method.

5 U.S. Patent No. 3,449,184 (Balk) teaches a method of preparing a laminated glass product by laminating an interlayer between two sheets of glass. Before lamination, each of the glass sheets and the interlayer are immersed in a bath of liquid resin. The glass sheets are then sandwiched against opposite faces of the interlayer, thereby trapping a small quantity of the resin therebetween. The resin then either absorbs into the interlayer  
10 or polymerizes to a solid state, depending on the materials used, thereby bonding the glass sheets together. Suitable polymerizable resins are stated to be epoxides, polyesters, vinyl monomers, and mixtures of the three. Exemplified interlayers include paper, cloth fabrics, metal foils, monofilaments, metallic flakes, and particulate materials.

In a particular embodiment, the interlayer is an organic plastic film. The interlayer  
15 may be a thermoplastic film, such as plasticized polyvinyl chloride, plasticized polyvinyl butyral (e.g., 15-50 parts plasticizer per hundred parts polyvinyl butyral), or plasticized ethyl cellulose (e.g., 10-100 parts plasticizer per hundred parts ethyl cellulose).

Alternatively, the interlayer may be a thermosetting film, such as a rubber elastomer or silicone elastomer compounded with crosslinking or vulcanizing materials. In this  
20 particular embodiment, the bath in which the film is immersed is that of a plasticizer for the film (e.g., triethylene glycol di(2-ethyl butyrate), dibutyl sebacate, or hexadecyl alcohol for polyvinyl butyral or ethyl cellulose plastic films or a silicone prepolymer, such as methyl silicone oil containing a curing agent, such as benzoyl peroxide, for silicone  
25 elastomer plastic films). After formation of the sandwich construction, the plasticizer is said to absorb into the organic plastic film. When the plasticizer is completely absorbed, after about one-half hour to several hours at room temperature, or faster if temperatures of about 60°C are used, the laminate is bonded together.

U.S. Patent No. 4,341,576 (Lewis) teaches a method of fabricating laminated safety glass without using an autoclave. Excess liquid plasticizer is applied to a sheet of  
30 plasticized interlayer material (i.e., polyvinyl butyral) by soaking at room temperature for a sufficient amount of time to "soften" surfaces of the plasticized interlayer material so that the interlayer becomes more amenable to adhesion to glass sheets, but not such a long time

that the plasticizer content is normalized throughout the thickness of the plasticized sheet. Large glass sheets are then assembled around opposite sides of the plasticized interlayer material. Excess plasticizer is removed by compressing the assembly. The assembly is then subjected to a temperature range above room temperature and below the temperature at which the plasticizer develops a volatile product. Simultaneously, the assembly is subjected to a superatmospheric pressure of not more than two atmospheres. U.S. Patent No. 4,385,951 (Pressau) teaches a modified version of a similar lamination method.

Many of the interlayers used in conventional methods are crystalline or semi-crystalline, displaying a measurable melting temperature when tested according to Differential Scanning Calorimetry (DSC). Such crystalline and semi-crystalline materials are more difficult to diffuse components into. Thus, as has been demonstrated, heat or pressure is often needed to obtain bonds having a wide variety of strengths, from pressure-sensitive to structural strengths, in a timely manner. There is a need for an efficient bonding method for all laminate articles.

There is also a particular need for laminate articles that are useful in optical applications where it is necessary or desirable to see through the laminate articles without a distorted view. Many of the currently used laminate articles suffer from environmental degradation (e.g., hydrolytic or oxidative instability), which decreases their long-term usefulness in optical applications. Thus, alternative laminate articles are needed.

20

### Summary of the Invention

A method for forming a laminate according to the present invention comprises the steps of: (a) providing a substrate comprising a surface to be bonded; (b) providing an amorphous polymeric film comprising a first major surface and a second major surface; (c) coating at least a portion of at least one of the substrate surface to be bonded and the first major surface of the polymeric film with a non-volatile plasticizer, wherein the non-volatile plasticizer is substantially non-reactive with itself; (d) positioning the first major surface of the polymeric film with the substrate surface to be bonded; and (e) forming an adhesive bond between the polymeric film and the substrate due to the absorption of the plasticizer into the polymeric film. In a further embodiment, at least one of the first major surface of the polymeric film and the substrate surface to be bonded is at least partially structured.

A further embodiment also comprises the steps of: (f) providing a second substrate; (g) coating at least a portion of at least one of the second substrate surface to be bonded and the second major surface of the polymeric film with a non-volatile plasticizer, wherein the non-volatile plasticizer is substantially non-reactive with itself; (h) positioning the second major surface of the polymeric film with the second substrate surface to be bonded; and (i) forming an adhesive bond between the polymeric film and the second substrate at essentially room temperature due to the absorption of the plasticizer into the polymeric film.

A wide variety of substrates can be used. For example, the substrate may be rigid or the substrate may be flexible. In optical applications, preferred substrates are transparent (e.g., glass or polymeric materials)

A wide variety of plasticizers can also be used. For example, the plasticizer may be a solid at room temperature. In this embodiment, the method further comprises the step of thermally activating the plasticizer. Alternatively, the plasticizer may be a liquid at room temperature. Preferably, the plasticizer is selected from the group consisting of monoalkyl esters of aliphatic carboxylic acids, monoalkyl esters of aromatic carboxylic acids, polyalkyl esters of aliphatic carboxylic acids, polyalkyl esters of aromatic carboxylic acids, polyalkyl esters of aliphatic alcohols, polyalkyl esters of phosphonic acids, poly(alkoxylated) esters of aliphatic carboxylic acids, poly(alkoxylated) esters of aromatic carboxylic acids, poly(alkoxylated) ethers of aliphatic alcohols, poly(alkoxylated) ethers of phenols, and mixtures thereof.

A wide variety of polymeric films can be used. For ease of handling, it is preferred that the polymeric film has a glass transition temperature of less than about 35°C. It is also preferred that the polymeric film has a glass transition temperature of greater than about -20°C. Examples of amorphous polymeric films include those comprising the following polymers: poly(meth)acrylates and copolymers derived from (meth)acrylate monomers, styrene-butadiene copolymers, polyvinyl esters and copolymers derived from vinyl ester monomers, and combinations thereof. Due to the widespread availability of (meth)acrylates and their ability to provide optical laminates, preferred polymeric films comprise a (meth)acrylate-derived polymer. Preferably, the polymeric film has a thickness of about 25 micrometers to about 500 micrometers.

The use of amorphous polymeric films enables more efficient absorption of the

plasticizer into the polymeric film. Advantageously, the adhesive bond can be formed at essentially room temperature. Another advantage is that the adhesive bond can be formed at essentially atmospheric pressure. These advantages allow the lamination method to be used without costly equipment and numerous processing steps. Many applications that were previously afflicted with air entrapment, and thus defects, in laminates used therein are able to be effectively bonded with fewer defects using the present method. For example, solar control films can be bonded to windows in buildings, providing essentially defect-free laminates. Timely bonding is also obtainable using the method of the invention. For example, the adhesive bond can be formed within about 30 minutes.

The method may be used for repairing transparent substrates having at least one blemish (e.g., scratch or abrasion) thereon. In this embodiment, the substrate surface to be bonded is a transparent substrate having at least one blemish thereon. Using the method of the invention, such a blemish can be made essentially invisible after bond formation.

Laminate articles can be prepared using the method of the invention. In one embodiment, a transparent substrate laminate comprises a plasticized polymeric film and a substrate having at least one blemish thereon that is repaired using the method of the invention. In another embodiment, an essentially defect-free laminate article comprises a substrate and a plasticized amorphous polymeric film comprising an amorphous polymer and a plasticizer dispersed throughout the amorphous polymer. The plasticizer is typically dispersed throughout the amorphous polymer due to absorption during bond formation. Preferably, the plasticizer is dispersed substantially uniformly throughout the plasticized polymeric film when bonding of the laminate is complete.

In yet another embodiment, an essentially defect-free optical laminate article comprises a substrate and a plasticized polymeric film comprising: a polymer selected from the group consisting of (meth)acrylate-derived polymers and vinyl ester-derived polymers and a plasticizer. The optical laminate may further comprise a second substrate, assembled such that the plasticized polymeric film is positioned between the substrate and the second substrate. In preferred embodiments thereof, the substrate and second substrate each individually comprise a material selected from the group consisting of glass and polymeric materials.

Kits of the invention can be used with the lamination method described herein. The kits typically comprise an amorphous polymeric film and a sufficient amount of a non-

volatile plasticizer for forming a laminate comprising the amorphous polymeric film and a substrate. The kits can be used for repair of transparent substrates. For example, blemishes on the surface of transparent substrates can be repaired such that the blemish is essentially invisible to the unaided human eye. For example, the transparent substrate, 5 upon repair, has an appearance similar to that of non-blemished portions of the substrate. According to one aspect of the invention, the amorphous polymeric film comprises a (meth)acrylate-derived polymer. According to another aspect of the invention, the amorphous polymeric film comprises a first major surface to be bonded to a first substrate and further comprises a second substrate to be bonded to a second major surface of the 10 polymeric film.

#### **Detailed Description of the Preferred Embodiments**

Laminated articles of the present invention are prepared using at least one substrate to be bonded, a polymeric film, and a plasticizer for coating at least one surface of the 15 substrate or polymeric film to be bonded. Upon absorption of the plasticizer into the polymeric film, a laminate article (also referred to simply as a laminate) is formed.

Laminated articles that are "essentially defect-free" are preparable using the method of the invention. "Defect-free" laminate articles are those that do not contain any entrapped air bubbles that are visible to the unaided human eye. Laminate articles of the 20 present invention are "essentially defect-free." The ability to provide laminate articles with reduced or no defects allows the laminate articles to be used effectively in optical applications. That is, "optical laminate articles" of the present invention are those through which a user can see with an essentially undistorted view.

Preferred embodiments of each of the invention are further described below:

25

#### Substrate

Any suitable substrate can be bonded using the present method. Suitable substrates can be of any Young's modulus and may be, for example, rigid (e.g., the substrate may be a 30 6 millimeter-thick sheet of plate glass) or flexible (e.g., the substrate may be a 37 micrometer-thick polyester film).

In one embodiment, a single substrate is laminated to a polymeric film. In another embodiment, two substrates are laminated around a polymeric film. For example, two

rigid substrates can be laminated together using the method of the invention. Two flexible substrates can be laminated together using the method of the invention. Alternatively, one rigid substrate and one flexible substrate can be laminated together using the method of the invention.

5        Further laminates can be prepared based on these embodiments. For example, a laminate assembly may comprise a first substrate, a polymeric film, a second substrate, a polymeric film, a third substrate, etc. in that order or in other configurations. Although it is preferred, it should be noted that each bond in a laminate (i.e., the bond at each interface) need not be formed using the method of the invention.

10      The substrates may be any suitable type of material. For example, substrates may be metal, ceramic, glass, polymeric, composites, and the like. The type of material used for the substrates generally depends on the application in which the laminate article will be used. As mentioned in the background, certain properties (e.g., transparency for optical applications) are needed when using laminate articles in particular applications.

15      In one preferred embodiment, the laminated articles are used in applications where it is desirable, or necessary, to see through the substrate. Thus, the substrates are typically transparent (e.g., glass or polymeric, typically glass or polycarbonate).

As with the type of material, the dimensions and surface topography of the substrates generally depend on the application in which the laminate article will be used.

20      The surface of the substrate to be bonded may be at least partially structured. For example, methods of structuring polymeric films of the invention are discussed infra, under the subsection "Polymeric Film." These same principles can be applied to structuring surfaces of substrates to be bonded.

25      The surface topography of a substrate may also be roughened in a non-structured way, such as by scratching or abrading (e.g., by vandalism). For example, transparent substrates (e.g., glass or polycarbonate) having at least one blemish (e.g., scratch or abrasion) described in copending U.S. Patent Application Serial No. 09/181,198, assigned to the assignee of the present application and entitled "Repaired Scratched and/or Abraded Transparent Substrates Having Protective Removable Sheets Thereon and a Method of Making," may be repaired by bonding a polymeric film and, optionally, one or more substrates thereto using the method of the invention. By "repaired" it is meant that the blemish is essentially invisible to the unaided human eye after bond formation.

Substrates having rough surface topographies (e.g., concrete pavement and woven fabrics) can be effectively laminated in accordance with the present invention. Typically, substrates having rough surface topographies are more difficult to bond due to their uneven surfaces, which may also make it more difficult to remove entrapped air bubbles from the laminate if the topography of the surface is not structured, or otherwise roughened, in configurations to allow for escape of air bubbles.

Preferably, the substrate does not compete effectively with the polymeric film in absorbing the plasticizer. That is, preferably the substrate does not absorb a significant amount of the plasticizer during bond formation, preventing an adhesive bond from forming. The type and amount of the plasticizer may also be adjusted to compensate for any absorption of the plasticizer by the substrate.

#### Plasticizer

Any suitable plasticizer may be used. The plasticizer is an organic compound that acts to increase flexibility and toughness of the polymeric film by internal modification (i.e., solvation) of the polymeric film. In contrast to adhesives, a plasticizer is not capable of forming a significant bond (i.e., a bond having a 180° peel adhesion value of greater than about 3 N/dm after aging for 30 minutes) by itself.

The plasticizer may be solid or liquid at room temperature and atmospheric pressure. If solid, the plasticizer can be softened or liquified, before, during, or after the laminate is assembled by thermal activation (e.g., heating) to cause the plasticizer to melt. If solid, the plasticizer is typically a crystalline solid, displaying a measurable melting temperature when measured using Differential Scanning Calorimetry (DSC). It is preferred that the melting temperature of solid plasticizers used in the present invention is relatively low (i.e., less than about 60°C) so as to minimize any heating that may be required in lamination methods of the present invention.

Preferably, however, the plasticizer is liquid at room temperature so that an elevated temperature step is not necessary. When plasticizers are used that are liquid at room temperature, heating is not required to cause the bond to form in a timely manner.

Viscosity of the plasticizer may be tailored for application. It is preferred that the viscosity of the plasticizer is sufficiently low to facilitate spreading of the plasticizer over the substrate surface to be bonded and to facilitate absorption of the plasticizer into the

polymeric film. Preferably, viscosity of the plasticizer is less than about 1,000 centiPoise (cP) when liquified, more preferably, the viscosity of the plasticizer is less than about 500 cP, and most preferably, less than about 200 cP when liquified.

It is preferred that the plasticizer is compatible with the polymeric film. When the 5 polymeric film is a blend of more than one polymer, it is preferred that the plasticizer is compatible with each polymer in the blend.

"Compatible" refers to a plasticizer that: (1) exhibits essentially no gross phase separation after absorption of the plasticizer into the polymeric film when the bond is formed, and (2) exhibits essentially no gross phase separation from the polymeric film 10 upon aging. By "phase separation" it is meant that by Differential Scanning Calorimetry (DSC), no detectable thermal transition, such as a melting or glass transition temperature can be found for the pure plasticizer in the polymeric film. Some migration of the plasticizer from or throughout the polymeric film can be tolerated, such as minor 15 separation due to composition equilibrium or temperature influences, but the plasticizer does not migrate to the extent of phase separation between the polymeric film and the plasticizer. Haziness may also be evidence of gross phase separation.

Compatibility of the plasticizer with the polymeric film helps to minimize the amount of time needed for bond formation. Furthermore, compatibility of the plasticizer with the polymeric film enhances long term effectiveness of the bond within the laminate 20 article.

It is also preferred that the plasticizer is non-volatile. "Non-volatile" refers to 25 plasticizers that do not substantially vaporize under bond formation conditions. That is, the plasticizers generate less than 3% VOC (volatile organic content). The VOC content can be determined analogously to ASTM D 5403-93 by exposing the plasticizer coated substrate or polymeric film to  $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$  in a forced draft oven for one hour. If less than 3% of the plasticizer is lost from the coating, then the plasticizer is considered "non-volatile." In contrast, water, for example, is a volatile plasticizer and evaporates under most bond formation conditions used in preferred embodiments of the present invention.

Preferably, the plasticizer is non-reactive with other components in the system or 30 atmospheric components. For example, preferably the plasticizer is inert with respect to other components in the system, including the substrate(s) and polymeric film. When the plasticizer is non-reactive with the other components, alteration (e.g., crosslinking) of the

structure of the substrates and polymeric film is minimized. When the plasticizer is non-reactive with respect to atmospheric components (e.g., oxygen), loss of optical properties, such as by hazing or yellowing, may be minimized.

Furthermore, the plasticizer is preferably non-reactive with itself. That is, 5 preferably the plasticizer is already substantially polymerized, if polymerization is to occur at all. This obviates the need for a subsequent polymerization step after assembling the laminate.

Useful plasticizers have a broad range of molecular weights and architectures. The 10 plasticizers may be polymeric or monomeric. Monomeric plasticizers are typically derived from mono- or multi-functional, low molecular weight acids or alcohols that are esterified with a mono-functional alcohol or mono-functional acid, respectively. Common among these monomeric plasticizers are esters of mono- or di-basic acids such as myristate esters, phthalate esters, adipate esters, phosphate esters, citrates, trimellitates, glutarates, and sebacate esters (e.g., dialkyl phthalates, such as dibutyl phthalate, diisooctyl phthalate, 15 dibutyl adipate, dioctyl adipate; 2-ethylhexyl diphenyl diphosphate; t-butylphenyl diphenyl phosphate; butyl benzylphthalates; dibutoxyethoxyethyl adipate; dibutoxypropoxypropyl adipate; acetyltri-n-butyl citrate; dibutylsebacate; etc.). Phosphate ester plasticizers are commercially sold under the trade designation SANTICIZER from Monsanto; St. Louis, MO. Glutarate plasticizers are commercially sold under the trade designation 20 PLASTHALL 7050 from C.P. Hall Co.; Chicago, IL.

Polymeric plasticizers are typically derived from cationic, free-radical, condensation, or ring-opening polymerizable monomers. If polymeric, the plasticizers are 25 typically relatively low molecular weight (i.e., preferably less than about 5,000, more preferably less than about 1,500 weight average molecular weight). In general, the lower the molecular weight of the plasticizer, the higher the compatibility of the plasticizer with the polymeric film. Common among polymeric plasticizers are polybutenes, polyvinylethers, polyethers (including polyalkylene oxides and functionalized polyalkylene oxides), polyesters, polymeric adipates (e.g., polyester adipates), polyols (e.g., glycerin), and the like. Polyester plasticizers are commercially sold under the trade designation 30 PARAPLEX from C.P. Hall Co.; Chicago, IL. Benzoyl-functionalized polyethers are commercially sold under the trade designation BENZOFLEX from Velsicol Chemicals; Rosemont, IL (e.g., BENZOFLEX 400, a polypropylene glycol dibenzoate). Alkyl-

functionalized polyalkylene oxides are commercially sold under the trade designation PYCAL from ICI Chemicals; Wilmington, DE (e.g., PYCAL 94, a phenyl ether of polyethylene oxide).

Preferably, the chemistry of the plasticizer is selected from the group consisting of 5 monoalkyl esters of aliphatic carboxylic acids, monoalkyl esters of aromatic carboxylic acids, polyalkyl esters of aliphatic carboxylic acids, polyalkyl esters of aromatic carboxylic acids, polyalkyl esters of aliphatic alcohols, polyalkyl esters of phosphonic acids, poly(alkoxylated) esters of aliphatic carboxylic acids, poly(alkoxylated) esters of aromatic carboxylic acids, poly(alkoxylated) ethers of aliphatic alcohols, poly(alkoxylated) ethers of phenols, and mixtures thereof.

The amount of plasticizer used depends on the materials comprising the substrates and polymeric film, as well as their dimensions. Generally, the amount of plasticizer used is up to about 50 milligrams per square centimeter of substrate area. Preferably from about 10 0.5 to about 10 milligrams per square centimeter is used to provide useful bonding times and minimize the change in physical properties (e.g., shear modulus) of the polymeric film.

While it is preferred that the plasticizer be used without further dilution, the plasticizer may be diluted in, for example, water or another solvent, preferably a solvent with a relatively high volatility (e.g., isopropanol and the like). Dilution can provide a 20 lower viscosity and more uniform spreading of the plasticizer onto the substrate. If diluted, a drying step is typically performed before the laminate is assembled.

#### Polymeric Film

Any suitable material can be used for the polymeric film. The polymeric film is 25 capable of absorbing the plasticizer when the plasticizer is in the liquid state. Upon absorption of the plasticizer, the polymeric film forms a measurable bond to the substrate. Preferably, the bond exhibits a 180° peel adhesion value of greater than about 3 N/dm after aging for 30 minutes. More preferably, the bond exhibits a 180° peel adhesion value of 30 greater than about 25 N/dm, even more preferably greater than about 40 N/dm, after aging for 30 minutes.

Preferably, the polymeric film is amorphous. That is, the amorphous polymeric film does not exhibit a measurable melting temperature when measured using Differential

Scanning Calorimetry (DSC). Amorphous polymeric films enable more rapid bond formation than many of their crystalline counterparts.

Typically, polymeric films prepared from free radically polymerizable monomers are amorphous. Thus, free radically polymerized polymeric films are preferred. Specific examples of polymeric films prepared as such include: poly(meth)acrylates and copolymers derived from (meth)acrylate monomers, styrene-butadiene copolymers, polyvinyl esters (e.g., polyvinyl acetates) and copolymers derived from vinyl ester (e.g., vinyl acetate) monomers, and the like.

Preferably, the polymeric film is a poly(meth)acrylate, copolymer derived from (meth)acrylate monomers, polyvinyl ester, or copolymer derived from vinyl ester monomers, as these materials tend to be the most environmentally stable (e.g., oxidation-resistant, hydrolysis-resistant, etc.) and when preparing laminate articles for use in applications where clarity is needed, they tend to provide the most optically clear laminate articles.

Due to their widespread availability, (meth)acrylate-derived polymers (i.e., (meth)acrylate polymers and copolymers derived from (meth)acrylate monomers) are preferred. In general, any (meth)acrylate monomers can be used to prepare the (meth)acrylate-derived polymers (including copolymers) can be used. Preferably, the number of carbons in the (meth)acrylate monomers is less than about 14, more preferably less than about 12. Longer carbon chains tend to result in more crystalline materials, which crystalline materials are not as preferred as their amorphous counterparts.

Any suitable styrene-butadiene copolymer may be used. Useful styrene-butadiene copolymer materials include those available from BASF Corporation, Charlotte, NC, under the trade designation, BUTOFAN, and those available from Mallard Creek Polymers, Inc., Charlotte, NC under the trade designation, ROVENE.

Any suitable vinyl ester-derived polymer (i.e., polyvinyl ester (e.g., polyvinyl acetate) or copolymers derived from vinyl ester monomers (e.g., vinyl acetate-ethylene copolymer)) may be used. Preferably, the comonomer content (e.g., ethylene content) is less than about 50% by weight in copolymers derived from vinyl ester monomers. Useful polyvinyl acetate materials include those available from Air Products; Allentown, PA under the trade designation, VINAC. Useful vinyl acetate-ethylene copolymer materials

include those available from Bayer Corporation; Akron, OH, under the trade designation, LEVAPREN.

The polymeric film may also comprise a blend of two or more polymers. If more than one polymer is used, preferably the polymers form a compatible blend having good optical clarity. "Compatible" blends are those that exhibit essentially no gross phase separation when blended together at room temperature and atmospheric pressure.

Preferably, the glass transition temperature ( $T_g$ ) of the polymeric film is close to the temperature at which the bond is formed. The  $T_g$  of the polymeric film is preferably less than about 60°C, more preferably less than about 50°C. Preferably, the bond is assembled at room temperature. Thus, preferably the  $T_g$  of the polymeric film is less than about 35°C. Although the polymeric film may be tacky, tackiness is not required. Thus, the  $T_g$  of the polymeric film may be greater than -20°C, more preferably greater than about 0°C. When the  $T_g$  is greater than about -20°C, the polymeric film may be more easily handled when assembly the laminate layers due to its relatively low tackiness.

The polymeric film may be crosslinked. However, to speed absorption of the plasticizer into the polymeric film, relatively low crosslinking is preferred. Crosslinking tends to decrease the absorption rate of plasticizer into a polymeric film.

Topography of the polymeric film may influence the absorption rate of the plasticizer. To increase the absorption rate, a structured surface may be used. For example, one or more surfaces of the polymeric film to be bonded can be at least partially structured (e.g., polymeric films having a microstructured surface), for example, such as those described in PCT Patent Publication No. WO 98/29,516, assigned to the present assignee and entitled, "Adhesives Having a Microreplicated Topography and Methods of Making and Using Same." Microreplication can be achieved by at least any of (1) casting the polymeric film using a tool having a microembossed pattern, (2) coating of the polymeric film onto a release liner having that microembossed pattern, or (3) passing through a nip roll to compress the polymeric film against a release liner having that microembossed pattern.

Desired embossing topography can be formed in tools via any of a number of well-known techniques, selected depending in part upon the tool material and features of the desired topography. Illustrative techniques include etching (e.g., via chemical etching, mechanical etching, or other ablative means such as laser ablation or reactive ion etching,

etc.), photolithography, stereolithography, micromachining, knurling (e.g., cutting knurling or acid enhanced knurling), scoring or cutting, etc. The presence of such surface structural topography can also beneficially impact the ability for air bubbles to escape from between laminate layers. As discussed above, air bubbles can undesirably lead to "defects" in the 5 final laminate article.

The structured topography can reside on a portion or all of at least one major surface of the polymeric film and can optionally reside on a portion or all of both major, opposing surfaces of the polymeric film affecting the properties of the interface(s) in the same or different manners, as desired by those skilled in the art. As discussed above, the 10 substrate surface to be bonded may be at least partially structured or otherwise roughened. When the substrate surface is at least partially structured, the polymeric film surface to be bonded may or may not also be at least partially structured or otherwise roughened.

The thickness of the polymeric film depends on the topography of the substrate being bonded. The polymeric film should be of sufficient thickness to absorb the 15 plasticizer and form a measurable bond to the substrate (i.e., a bond having a 180° peel adhesion of greater than about 3 N/dm after aging for 30 minutes). The polymeric film is typically greater than about 10 micrometers thick. Generally, the polymeric film is also about 1,000 micrometers thick or less. Preferably, the polymeric film has a thickness of about 25 to about 500 micrometers.

The polymeric film may contain any suitable additive. For example, the polymeric film may include further plasticizers and tackifiers. Plasticizers and tackifiers can lower the modulus of the film and thus, increase the absorption rate of the bonding plasticizer into the polymeric film. Use of such additives may depend on the particular application. For example, when longer bonding times are desired (e.g., when multiple repositioning is 25 needed after activation of the bonding mechanism), the use of tackifiers and plasticizers may not be preferred. Those of ordinary skill in the art can determine the suitability of particular additives for their particular application. A wide variety of other additives known to those skilled in the art, for example, adhesion promoters, can also be used in the polymeric film.

Bonding

Depending on the composition and thickness of the polymeric film, the composition and amount of plasticizer used, the composition and surface structure of the substrate, and other factors, the bonding time can be as short as several seconds or up to 5 one day. Any suitable method of forming a laminate from the materials of the invention can be used.

Advantageously, preferred embodiments of the invention do not require the use of elevated temperatures (i.e., those above 60°C, or in most preferred embodiments, those above room temperature (about 25°C)) for timely bonding. Although timely bonding may 10 differ depending on the application and the user's desires, for purposes of describing this invention timely bonding is about 12 hours or less, more preferably about 8 hours or less, even more preferably about 4 hours or less, even more preferably about 1 hour or less, and most preferably less than about 30 minutes.

Also, preferred embodiments of the invention do not require the use of non-atmospheric pressure, such as that provided by an autoclave or otherwise. Preferred 15 embodiments of the invention include those where lamination occurs at essentially atmospheric pressure. This enables lamination to easily occur in certain applications where essentially defect-free lamination was previously impossible (e.g., bulk structures, such as windows in buildings, etc.). However, increased/decreased pressure may be used 20 if desired.

In methods of the invention, at least one major surface of the substrate or the polymeric film is coated with the plasticizer. In certain embodiments, each of the major substrate surface and the major surface of the polymeric film is coated with the plasticizer. Any suitable coating method can be used. For example, the plasticizer may be applied to 25 the surface of the substrate or polymeric film to be bonded by: spraying, brushing, pouring, dripping, etc. the plasticizer onto the surface to be bonded.

To assemble the laminate, the substrate is positioned with the polymeric film such that at least one of the plasticizer-coated surfaces resides at the substrate/polymeric film interface. When laminating more than two substrates, a polymeric film is placed between 30 at least one set of adjacent substrates. However, more than one polymeric film may be used (e.g., when multiple substrate/polymeric film interfaces are bonded using the method of the invention). For example, a first polymeric film may be placed between a first and

second substrate and a second polymeric film may be placed between the second substrate and a third substrate.

In preferred embodiments, when multiple substrates are laminated together, at least two, most preferably all, of each substrate/polymeric film interfaces are bonded using the method of the invention. The plasticizer used at each interface may or may not be the same, both in terms of chemistry and amount. Furthermore, the substrates and polymeric films may or may not be the same throughout the entire laminate.

It should be noted that, although it is preferred to use the lamination method of the present invention, only one substrate/polymeric film interface need be present and bonded according to the invention. Further substrates may be bonded to the substrate and/or polymeric film using any suitable bonding method. For example, other bonding methods include those using mechanical (e.g., nails, rivets, etc.), chemical (e.g., adhesives, etc.), and physical (e.g., ultrasonic welding, etc.) means.

To form the bond, preferably excess air and plasticizer is squeezed from the substrate/polymeric film interface or multiple substrate/polymeric film interfaces. The excess air and plasticizer may be squeezed from the interface by using no more than hand pressure. Preferably, however, a squeegee or roller is applied to the sandwich assembly to remove the excess air and plasticizer. Preferably, no visible air bubbles remain in the assembled laminate article for optical laminate articles of the invention.

After assembly, an adhesive bond forms between the substrate and polymeric film. Migration (also referred to as absorption or diffusion) of the plasticizer into the bulk polymeric film facilitates bond formation. Thus, as discussed above, it is preferred that migration of the plasticizer is enabled and enhanced by using an amorphous polymeric film. This enables laminates to be formed at atmospheric pressure without the use of elevated temperatures. Further preferred for enhancing migration of the plasticizer into the bulk polymeric film is the use of a plasticizer that is compatible with the polymeric film. Preferably, the plasticizer is dispersed substantially uniformly throughout the plasticized polymeric film when bonding of the laminate is complete.

It is believed that the storage modulus at the surface of the polymeric film decreases during bond formation, typically to a value lower than that of the Dahlquist criterion (Sung Gun Chu, Chapter 8, Handbook of Pressure Sensitive Adhesive Technology, Second Edition, Donatas Satas, Editor, 1989). Upon migration of the

plasticizer into the bulk polymeric film, the storage modulus then increases to its equilibrium value. The resulting laminate article includes a polymeric film adhesively bonded to at least one major surface of at least one substrate.

Kits of the invention are particularly useful for practicing the method of the invention. The kits typically comprise a polymeric film, preferably an amorphous polymeric film, and a sufficient amount of a plasticizer (preferably a non-volatile plasticizer) for forming a laminate comprising the polymeric film and a substrate. To be sufficient, the amount of plasticizer must be great enough to form measurable bond between a first major surface of the polymeric film and substrate. The kits may further comprise a substrate to be bonded to a second major surface of the polymeric film.

### Articles

Laminate articles of the present invention can be used in a wide variety of applications. As described above, bonds at interfaces in the laminate may have a wide variety of strengths, from pressure-sensitive to structural strengths can be formed in a timely manner using materials and methods of the invention. "Pressure-sensitive" strengths are those that are about 3 N/dm to about 300 N/dm upon complete bond formation, as measured using a 90° peel adhesion test. "Structural" strengths are those that are greater than about 300 N/dm upon complete bond formation, as measured using a 90° peel adhesion test.

Particularly preferred laminate articles are optical laminate articles. That is, they can be used in application where it is desired or necessary to be able to see through the laminate article without a distorted view. For example, computer screens, television screens, automobile windows, architectural windows, and a wide variety of other applications can benefit from the present invention. As discussed in the polymeric film section, preferred polymeric film materials for use in laminate articles are poly(meth)acrylates and copolymers derived from (meth)acrylate monomers, as well as polyvinyl esters and copolymers derived from vinyl ester monomers.

A number of other laminate articles can be prepared using the method of the present invention. These laminate articles and applications for their use are readily apparent to those of ordinary skill in the art. Certain embodiments of the invention are

illustrated in the examples below. Many other variations of the invention are also within the scope of the appended claims.

## EXAMPLES

5 This invention is further illustrated by the following examples that are not intended to limit the scope of the invention. In the examples, all parts, ratios and percentages are by weight unless otherwise indicated. All materials used in the Examples are commercially available from Aldrich Chemicals (Milwaukee, WI), unless otherwise indicated or described.

10

### Test Methods

In order to test adhesion resulting from plasticizer-assisted lamination with various polymeric film/plasticizer pairs, the following adhesion test was carried out:

15 A clean glass plate was uniformly coated with a 10% solids isopropanol solution of plasticizer using a #12 wire wound rod, resulting in a 27-micron thick wet plasticizer coating. The coating was air-dried at room temperature to nominally give a 2.7 micron thick coating (approximately  $0.3 \text{ mg/cm}^2$ ) of the dried plasticizer film.

20 A 12.7-millimeter wide strip of a polyester backing coated with a transparent polymeric film was laminated to the dried plasticizer film using a 1.8-kilogram rubber roller. After dwelling at room temperature for 30 minutes, the free end of the polymer-coated polyester backing was doubled back nearly touching itself, so that the angle of removal was  $180^\circ$ . The free end was then attached to an adhesion tester scale.

25 The glass test plate was clamped in the jaws of a tensile testing machine that was capable of moving the plate away from the scale at a constant rate of 2.3 meters/minute. The scale reading was recorded in Newtons as the tape was peeled from the glass surface and the adhesion failure mode was noted. The peel adhesion data was reported as the average of the range of numbers observed during the test. Unless specified, all failures were adhesive from the glass plate. Other failures were denoted as follows:

30 coh = cohesive failure  
part coh = partially cohesive, partially adhesive failure  
del = polymeric film delaminated from polyester backing  
part del = polymeric film partially delaminated from polyester backing

sh = failed adhesively in a shocky fashion

### Polymeric Films

The polymeric film samples used in these examples were prepared and tested in the  
5 following manner. Test results are provided in Table 2.

#### Polymeric Film 1

ROVENE 9413 (a carboxylated styrene-butadiene emulsion polymer, commercially available from Rohm and Haas; Spring House, PA) was knife-coated onto a  
10 37-micrometer thick polyester backing to provide a polymeric film having a thickness of 64 micrometers after drying at 65° C for 10 minutes and conditioning for 24 hours at 23°C and 50% relative humidity. Performance in plasticizer-assisted lamination was assessed with the test method described above using the plasticizers found in Table 1.

#### 15 Polymeric Film 2

A 90/10 (weight ratio) n-butyl acrylate/acrylic acid (nBA/AA) solution copolymer was prepared by charging 18 grams butyl acrylate and 2 grams acrylic acid into a 100 mL glass bottle along with a solution of 0.06 gram VAZO 64 (a 2,2'-azo-bis(isobutyronitrile) initiator, commercially available from E.I. duPont de Nemours & Co.; Wilmington, DE) in  
20 30 grams of acetone.

After purging the headspace with nitrogen, the bottle was sealed and placed in a rotating constant temperature bath for 16 hours at 55°C. The resulting copolymer solution was diluted to 31.5% solids with additional acetone, then knife-coated to a dry polymeric film having a thickness of 46 micrometers onto a 37-micrometer thick polyester backing  
25 after drying at 65° C for 10 minutes and conditioning for 24 hours at 23°C and 50% relative humidity. Performance in plasticizer-assisted lamination was assessed with the test method described above using the plasticizers found in Table 1.

#### Polymeric Film 3

30 A 98/2 (weight ratio) ethyl acrylate/acrylic acid (EA/AA) solution copolymer was prepared following the procedure in Polymeric Film 2, except ethyl acetate solvent was used as the solvent. After diluting to 20% solids with ethyl acetate, the resulting solution

was coated to provide a polymeric film having a thickness of 23 micrometers after drying at 65° C for 10 minutes and conditioning for 24 hours at 23°C and 50% relative humidity. Performance in plasticizer-assisted lamination was assessed with the test method described above using the plasticizers found in Table 1.

5

#### Polymeric Film 4

ELVACE 734 (a vinyl acetate-ethylene emulsion polymer, commercially available from Reichhold; Research Triangle Park, NC) was knife-coated onto a 37-micrometer thick polyester backing to a dry polymeric film having a thickness of 66 micrometers after 10 drying at 65° C for 10 minutes and conditioning for 24 hours at 23°C and 50% relative humidity. Performance in plasticizer-assisted lamination was assessed with the test method described above using the plasticizers found in Table 1.

#### Polymeric Film 5

15 Into a 100 mL glass jar charged with 10 grams LEVAPREN 500 (a vinyl acetate-ethylene copolymer, commercially available from BASF; Mt. Olive, NJ) and 15 grams FORAL 85 (a glycerine rosin ester tackifying resin, commercially available from Hercules, Inc.; Wilmington, DE), 83.3 grams toluene was added. After rolling for 16 hours at room temperature on a ball mill, the resulting solution was coated onto a polyester backing to produce a dry polymeric film having a thickness of 33 micrometers after drying at 65° C 20 for 10 minutes and conditioning for 24 hours at 23°C and 50% relative humidity. Performance in plasticizer-assisted lamination was assessed with the test method described above using the plasticizers found in Table 1.

25

#### Polymeric Film 6

A 96/4 (weight ratio) isoctyl acrylate/acrylamide (IOA/Acm) solution copolymer was prepared following the procedure in Polymeric Film 2. After diluting to 20% solids with acetone, the resulting solution was coated to provide a dry polymeric film having a thickness of 23 micrometers after drying at 65° C for 10 minutes and conditioning for 24 30 hours at 23°C and 50% relative humidity. Performance in plasticizer-assisted lamination was assessed with the test method described above using the plasticizers found in Table 1.

**Polymeric Film 7**

Into a 200 mL glass jar charged with 22.5 grams of an 80/18/2 poly(vinylbutyral-co-vinyl alcohol-co-vinyl acetate) copolymer having a molecular weight of 90,000-120,000 (commercially available from Aldrich Chemical; Milwaukee, WI), 63.8 grams 5 ethanol and 63.8 grams toluene were added. After rolling for 16 hours at room temperature on a ball mill, the resulting homogeneous solution was coated to provide a polymeric film having dry thickness of 13 micrometers after drying at 65° C for 10 minutes and conditioning for 24 hours at 23°C and 50% relative humidity. Performance in plasticizer-assisted lamination was assessed with the test method described above using 10 the plasticizers found in Table 1.

**Plasticizers**

The plasticizers listed in Table 1 were coated, dried, laminated to the polymeric film samples and tested for adhesion as described above.

Table 1

| No. | Trade Designation  | Chemical Name                                    | Source                                  |
|-----|--------------------|--|---|
| A   | KODAFLEX DOA       | Dioctyl adipate                                  | Eastman Chemicals Co.;<br>Kingsport, TN |
| B   | CITRAFLEX A-6      | acetyl trihexyl citrate                          | Morflex; Greensboro, NC                 |
| C   | BENZOFLEX<br>P-200 | PEG 200 dibenzoate                               | Velsicol Chemical Co.;<br>Rosemount, IL |
| D   | TONE 0201          | Polycaprolactone diol                            | Union Carbide Corp.;<br>Danbury, CT     |
| E   | BENZOFLEX 9-88     | Dipropylene glycol<br>dibenzoate                 | Velsicol Chemical Co.;<br>Rosemount, IL |
| F   | PLASTILIT 3060     | Propoxylated alkyl<br>phenyl ether               | BASF; Mt. Olive, NJ                     |
| G   | SANTICIZER 154     | t-butylphenyl phenyl<br>phosphate                | Monsanto Co; St. Louis, MO              |
| H   | IGEPAL CO-730      | Ethoxylated nonylphenol                          | Rhone Poulenc; Cranbury, NJ             |
| I   | SPAN 85            | Sorbitan trioleate                               | ICI Americas; Wilmington, DE            |
| J   | TWEEN 21           | PEG-4 sorbitan<br>monolaurate                    | ICI Americas; Wilmington, DE            |
| K   | SANTICIZER 160     | butyl benzyl phthalate                           | Monsanto Co.; St. Louis, MO             |
| L   | TERGITOL 15-S-9    | ethoxylated (9 EO) C <sub>13-15</sub><br>alcohol | Union Carbide Corp.;<br>Danbury, CT     |
| M   | BUTYL<br>STEARATE  | butyl stearate                                   | Eastman Chemical Co.;<br>Kingsport, TN  |
| N   | KODAFLEX DOP       | dioctyl phthalate                                | Eastman Chemical Co.;<br>Kingsport, TN  |
| O   | SANTICIZER 141     | 2-ethylhexyl diphenyl<br>phosphate               | Monsanto Co.; St. Louis, MO             |
| P   | ADOL 66            | isostearyl alcohol                               | Sherex; Dublin, OH                      |
| Q   | TEGMER 804         | tetraethylene glycol di-2-<br>ethylhexanoate     | C.P. Hall, Co.; Chicago, IL             |
| R   | PLASTHALL 205      | dibutoxyethyl azelate                            | C.P. Hall, Co.; Chicago, IL             |

Table 2

| Plasti-<br>cizer<br>No. | Peel Adhesion (N/dm)  |                  |                   |                   |                  |      |     |
|-------------------------|-----------------------|------------------|-------------------|-------------------|------------------|------|-----|
|                         | (Failure Mode)        |                  |                   |                   |                  |      |     |
|                         | Polymeric Film Number |                  |                   |                   |                  |      |     |
|                         | 1                     | 2                | 3                 | 4                 | 5                | 6    | 7   |
| A                       | 58                    | 77               | 28                | 0                 | 65               | 38   | 0   |
| B                       | 10                    | 18<br>(coh)      | 8.3<br>(part coh) | *<br>(del)        | 31<br>(part coh) | 29   | 0   |
| C                       | 9                     | 47               | 19                | 1.3<br>(part del) | 61               | 29   | 0   |
| D                       | 0                     | 27               | 3.5               | 7.4               | 0                | 0    | 0   |
| E                       | 44                    | 45               | 4.6               | *<br>(del)        | 73               | 42   | 0   |
| F                       | 34                    | 57               | 50                | 0                 | 55               | 37   | 1.3 |
| G                       | 13                    | 55               | 7.2               | *<br>(del)        | 63               | 39   | 0   |
| H                       | 0                     | 46               | 13                | 0                 | 0                | 0    | 0   |
| I                       | 0                     | *                | 0                 | 0                 | 16<br>(sh)       | 10.5 | 0   |
| J                       | 0                     | 45               | 0                 | 0                 | 0                | 0    | 0   |
| K                       | 52                    | 65               | 46                | 0.7               | 51               | 43   | 0   |
| L                       | 0                     | 41               | 1.8               | 0                 | 26               | 2.4  | 0   |
| M                       | 18                    | 43<br>(part coh) | 0                 | 0                 | 53               | 15   | 0   |
| N                       | 15                    | *                | 28                | 0                 | 55               | 29   | 0   |
| O                       | 73                    | 71               | 54                | 0.7               | 70               | 37   | 2   |
| P                       | 21                    | 58               | 25                | 0                 | 71               | 39   | 0   |
| Q                       | 8.5                   | 57               | 35                | 0                 | 67               | 27   | 0   |
| R                       | 2.4                   | 55               | 40                | 1.8               | 56               | 15   | 0   |

\* Not Available

**Polymeric Films 8 through 14:**

A series of isoocetyl acrylate (IOA)/isobornyl acrylate (IBOA)/acrylic acid (AA) terpolymers were polymerized using ultraviolet polymerization. Specifically, a 90/10 IOA/AA copolymer (**Polymeric Film 8**) was prepared by blending 45 grams IOA monomer with 5 grams AA monomer and 0.1 gram IRGACURE 651 (a 2,2-dimethoxy-2-phenylacetophenone photoinitiator, commercially available from Ciba Specialty Chemicals Corp; Tarrytown, NY) in a 100 mL jar.

After purging vigorously with 5 liters/minute nitrogen for 10 minutes, partial polymerization to a coatable viscosity was initiated by brief exposure to the light from blacklight fluorescent bulbs (GE F40BL lamp, commercially available from GE Co.; Schenectady, NY).

A portion of the resulting moderate viscosity, partially polymerized fluid was coated to a thickness of 45 micrometers between a 37-micrometer thick polyester film and a 51-micrometer thick siliconized polyester release liner. The resulting assembly was further exposed to the fluorescent bulbs for 10 minutes to complete polymerization.

Similarly prepared were a 45/45/10 IOA/IBOA/AA terpolymer (**Polymeric Film 11**) and a 90/10 IBOA/AA copolymer (**Polymeric Film 14**).

A 75/15/10 IOA/IBOA/AA terpolymer (**Polymeric Film 9**) was prepared by blending 10 grams of the fluid from Polymeric Film 8 with 5 grams of the fluid from Polymeric Film 11.

A 60/30/10 IOA/IBOA/AA terpolymer (**Polymeric Film 10**) was prepared with 5 grams of the fluid from Polymeric Film 8 and 10 grams of the fluid from Polymeric Film 11.

Similarly prepared were 30/60/10 IOA/IBOA/AA (**Polymeric Film 12**) and 15/75/10 IOA/IBOA/AA (**Polymeric Film 13**) terpolymers using the fluids from Polymeric Films 11 and 14.

The polymer films were tested following the procedure described above using a select group of plasticizers from Table 1. Results are shown in Table 3.

Table 3

| Polymeric<br>Film<br>Number<br>(Composi-<br>tion) | Peel Adhesion (N/dm)             |                          |                          |                          |            |
|---|----------------------------------|--------------------------|--------------------------|--------------------------|------------|
|   | (Failure Mode)                   |                          |                          |                          |            |
|   | Plasticizer Number (Description) |                          |                          |                          |            |
|   | A<br>(KODAFLEX<br>DOA)           | E<br>(BENZOFLEX<br>9-88) | F<br>(PLASTILIT<br>3060) | O<br>(SANTICIZER<br>141) | None       |
| 8<br>(90/10<br>IOA/AA)                            | 76                               | 77                       | 73                       | 65                       | 87         |
| 9<br>(75/15/10<br>IOA/IBOA/<br>AA)                | 90                               | 84                       | 88                       | 66                       | 55<br>(sh) |
| 10<br>(60/30/10<br>IOA/IBOA/<br>AA)               | 103<br>(sh)                      | 82                       | 96                       | 72                       | 4.6        |
| 11<br>(45/45/10<br>IOA/IBOA/<br>AA)               | *                                | 96                       | 140                      | 95                       | 1.1        |
| 12<br>(30/60/10<br>IOA/IBOA/<br>AA)               | *                                | *                        | *                        | *                        | 0          |
| 13<br>(15/75/10<br>IOA/IBOA/<br>AA)               | *                                | *                        | *                        | *                        | 0          |
| 14<br>(90/10<br>IBOA/AA)                          | *                                | *                        | *                        | *                        | 0          |

\* Not Available

**Examples 15 through 20:** A series of glass plates were coated with solutions of PLASTILIT 3060 plasticizer in isopropanol that varied in plasticizer concentration from 0% to 40%. These coatings were made using a #12 wire wound rod, yielding coating weights from 0 to 1.2 mg/cm<sup>2</sup>. Selected polymeric film samples were laminated to these glass plates and the peel adhesion for each example was measured as described above. Results of these tests are shown in Table 4.

**Table 4**

| Ex. | Polymeric<br>Film | Plasticizer Concentration<br>(Failure Mode) |       |       |       |            |     |
|-----|-------------------|---|-------|-------|-------|------------|-----|
|     |                   | 0%  | 2%    | 5%    | 10%   | 20%        | 40% |
| 15  | 1                 | 19  | 42    | 15    | 51    | 12         | 5.0 |
| 16  | 2                 | 71  | 70    | 65    | 62    | 60         | 53  |
| 17  | 3                 | 48  | 53    | 49    | 44    | 22         | 12  |
| 18  | 5                 | *   | *     | 68    | 66    | 63         | 54  |
|     |                   | (del)                                       | (del) |       |       |            |     |
| 19  | 10                | 3.8   | del   | 97    | 93    | 92         | 54  |
| 20  | 11                | 0.4   | 17    | *     | *     | 197        | 59  |
|     |                   |   |       | (del) | (del) | (part coh) |     |

10 \* Not Available

**Examples 21 and 22:** An 80/20 IBOA/AA copolymer containing 40% added TERGITOL 15-S-9 plasticizer (Plasticizer L) was prepared by blending 48 grams IBOA monomer with 12 grams AA monomer, 40 grams of TERGITOL 15-S-9 and 0.08 grams IRGACURE 651. After purging and partial polymerization by exposure to light as described above for Polymeric Films 8 through 14, the resulting fluid was degassed by placing in a vacuum desiccator for one hour.

15 The composition was coated to a thickness of 90 micrometers between a 180 micrometer-thick, louvered cellulose (acetate-co-butyrate) privacy film (similar to those described in U.S. Patent No. 5,254,388) and a 51 micrometer-thick, siliconized polyester release liner.

After further exposure to the fluorescent bulbs to complete polymerization, the opposite side of the louvered film was similarly coated with a 90 micrometer-thick coating of the composition to give a coating (Polymeric Film 15) on each side.

5 A second doubly coated louvered film (Polymeric Film 16) was similarly prepared using a terpolymer of 35/55/10 butyl acrylate (BA)/IBOA/AA containing 20% added SANTICIZER 141 (Plasticizer O).

The siliconized polyester release liner was removed from one side of each construction, which was then laminated onto a puddle of plasticizer on a clean glass plate (14.0 centimeters by 15.2 centimeters). Excess plasticizer and trapped air was squeegeed 10 out and the second siliconized polyester release liner was removed from the side of the polymeric film-coated louvered privacy film opposite to the side laminated to the glass plate.

A puddle of plasticizer was poured at one end of each exposed polymeric film and a second clean glass plate was pivoted down onto each polymeric film surface, allowing 15 the fluid front to exhaust the air. Adjustment was made as necessary to align the assembly. Clamps were placed at the edges.

After sitting overnight, the plasticizer was absorbed into each of the polymeric films and bonds formed to the glass. The clamps were removed and the edges of the polymeric films trimmed with a razor blade.

20 The same plasticizer present in the composition was used in the lamination step for each construction (Example 21: Polymeric Film 15 and Plasticizer L; Example 22: Polymeric Film 16 and Plasticizer O).

The resulting laminates were evaluated in a cyclic temperature-humidity test involving 10 cycles of two hours at 25°C, 47.5% relative humidity; four hours at 65°C, 25 92.5% relative humidity; and eleven hours at 65°C, 47.5% relative humidity. The laminates maintained their essentially defect-free characteristics after such vigorous testing.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and principles of this invention, 30 and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth hereinabove.

What Is Claimed Is:

1. A method for forming a laminate, the method comprising the steps of:
  - providing a substrate having a surface to be bonded;
  - providing an amorphous polymeric film comprising a first major surface and a second major surface;
  - coating at least a portion of at least one of the substrate surface to be bonded and the first major surface of the polymeric film with a non-volatile plasticizer, wherein the non-volatile plasticizer is substantially non-reactive with itself;
  - positioning the first major surface of the polymeric film with the substrate surface to be bonded; and
  - forming an adhesive bond between the polymeric film and the substrate due to the absorption of the plasticizer into the polymeric film.
2. The method of claim 1, wherein the adhesive bond is formed at essentially room temperature.
3. The method of claim 1, wherein the adhesive bond is formed within about 30 minutes.
4. The method of claim 1, further comprising the steps of:
  - providing a second substrate having a surface to be bonded;
  - coating at least a portion of at least one of the surface to be bonded on the second substrate and the second major surface of the polymeric film with a non-volatile plasticizer, wherein the non-volatile plasticizer is substantially non-reactive with itself;
  - positioning the second major surface of the polymeric film with the surface to be bonded on the second substrate; and
  - forming an adhesive bond between the polymeric film and the second substrate at essentially room temperature due to the absorption of the plasticizer into the polymeric film.
5. The method of claim 1, wherein the substrate is rigid.

6. The method of claim 1, wherein the substrate is flexible.
7. The method of claim 1, wherein the plasticizer is a solid at room temperature.
- 5 8. The method of claim 7, further comprising the step of thermally activating the plasticizer.
9. The method of claim 1, wherein the plasticizer is a liquid at room temperature.
- 10 10. The method of claim 1, wherein the plasticizer is selected from the group consisting of monoalkyl esters of aliphatic carboxylic acids, monoalkyl esters of aromatic carboxylic acids, polyalkyl esters of aliphatic carboxylic acids, polyalkyl esters of aromatic carboxylic acids, polyalkyl esters of aliphatic alcohols, polyalkyl esters of phosphonic acids, poly(alkoxylated) esters of aliphatic carboxylic acids, poly(alkoxylated) esters of aromatic carboxylic acids, poly(alkoxylated) ethers of aliphatic alcohols, poly(alkoxylated) ethers of phenols, and mixtures thereof.
- 15 11. The method of claim 1, wherein the polymeric film has a thickness of about 25 micrometers to about 500 micrometers.
- 20 12. The method of claim 1, wherein the adhesive bond is formed at essentially atmospheric pressure.
- 25 13. The method of claim 1, wherein the polymeric film has a glass transition temperature of less than about 35°C.
14. The method of claim 1, wherein the polymeric film has a glass transition temperature of greater than about -20°C.
- 30 15. The method of claim 1, wherein the polymeric film comprises a material selected from the group consisting of poly(meth)acrylates and copolymers derived from

(meth)acrylate monomers, styrene-butadiene copolymers, polyvinyl esters and copolymers derived from vinyl ester monomers, and combinations thereof.

16. The method of claim 1, wherein the polymeric film comprises a (meth)acrylate-derived polymer.

17. The method of claim 1, wherein at least one of the first major surface of the polymeric film and the substrate surface to be bonded is at least partially structured.

10 18. The method of claim 1, wherein the substrate surface to be bonded is a transparent substrate having at least one blemish thereon.

19. The method of claim 18, wherein the blemish is essentially invisible after bond formation.

15 20. A laminate article prepared according to the method of claim 1.

21. A transparent laminate comprising:  
a transparent plasticized polymeric film; and  
20 a transparent substrate that is repaired using the method of claim 18.

22. An optical laminate article comprising:  
a substrate; and  
a plasticized polymeric film comprising:  
25 a polymer selected from the group consisting of (meth)acrylate-derived polymers and vinyl ester-derived polymers, and  
a plasticizer,

wherein the optical laminate article is essentially defect-free.

30 23. The laminate article of claim 22, further comprising a second substrate, assembled such that the plasticized polymeric film is positioned between the substrate and the second substrate.

24. The laminate article of claim 22, wherein the substrate and second substrate each individually comprise a material selected from the group consisting of glass and polymeric materials.

5      25. A laminate article comprising:  
          a substrate; and  
          a plasticized amorphous polymeric film comprising:  
                an amorphous polymer, and  
                a plasticizer dispersed throughout the amorphous polymer,  
10     wherein the laminate article is essentially defect-free.

26. A kit comprising:  
          an amorphous polymeric film; and  
          a sufficient amount of a non-volatile plasticizer for forming a laminate  
15     comprising the amorphous polymeric film and a substrate.

27. The kit of claim 26, wherein the kit is for repair of transparent substrates having at least one blemish thereon.

20     28. The kit of claim 26, wherein the amorphous polymeric film comprises a (meth)acrylate-derived polymer.

25     29. The kit of claim 26, wherein the amorphous polymeric film comprises a first major surface to be bonded to a first substrate and further comprising a second substrate to be bonded to a second major surface of the polymeric film.

**INTERNATIONAL SEARCH REPORT**

|                              |
|------------------------------|
| International Application No |
| PCT/US 99/06016              |

|   |   |   |  |  |
|---|---|---|--|--|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b>  |   |   |  |  |
| IPC 7 B32B17/10 B32B27/22 B32B7/04 C08J5/12 B32B31/00   |   |   |  |  |
| According to International Patent Classification (IPC) or to both national classification and IPC   |   |   |  |  |
| <b>B. FIELDS SEARCHED</b>   |   |   |  |  |
| Minimum documentation searched (classification system followed by classification symbols)   |   |   |  |  |
| IPC 7 B32B B29C C08J  |   |   |  |  |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched   |   |   |  |  |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  |   |   |  |  |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>   |   |   |  |  |
| Category  | Citation of document, with indication, where appropriate, of the relevant passages      | Relevant to claim No.                     |  |  |
| X   | US 4 358 329 A (MASUDA EISUKE)<br>9 November 1982 (1982-11-09)                          | 1,4-6,<br>8-10,<br>13-15,<br>20-24        |  |  |
| X   | column 7, line 47; claims 1-3,5,8-10;<br>example 1                                      | 2,3,11,<br>12<br>26,28,29                 |  |  |
| A   | ---   | 18,19,27                                  |  |  |
| X   | US 4 385 951 A (PRESSAU JEAN P)<br>31 May 1983 (1983-05-31)<br>cited in the application | 1,2,4,5,<br>7,8,10,<br>12,15,<br>18,20-24 |  |  |
| A   | column 5, line 1-19 -column 6, line 54-68;<br>claims 1,5-7; examples<br>---             | 25-27,29                                  |  |  |
|   | -/-   |   |  |  |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.   |   |   |  |  |
| * Special categories of cited documents :<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed  |   |   |  |  |
| "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<br>"&" document member of the same patent family |   |   |  |  |
| Date of the actual completion of the international search   | Date of mailing of the international search report                                      |   |  |  |
| 4 November 1999   | 28.02.2000  |   |  |  |
| Name and mailing address of the ISA   | Authorized officer  |   |  |  |
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl<br>Fax: (+31-70) 340-3016  | DERZ T.   |   |  |  |

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/06016

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.           |
|----------|--|---------------------------------|
| X        | US 4 341 576 A (LEWIS CHARLES W)<br>27 July 1982 (1982-07-27)<br>cited in the application<br>claims 1,2,7<br>---                                 | 1,2,4,5,<br>7,8,10,<br>15,20-24 |
| X        | US 3 449 184 A (BALK ALBERT C)<br>10 June 1969 (1969-06-10)<br>cited in the application<br>column 4, line 56-65; claims<br>1,4,5,10-12,15<br>--- | 1,4,5,<br>10,15,<br>20-24       |
| X        | US 4 386 991 A (SHIOMI TEIICHI ET AL)<br>7 June 1983 (1983-06-07)<br>column 3-4; claims 1,3,5<br>-----   | 1,2,5,9,<br>12,15,<br>20-22,24  |

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 99/06016

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-24, 26-29

#### Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-24, 26-29

bonding of a polymer film to a substrate  
by applying liq. NON-VOLATILE, NON-REACTIVE plasticiser to  
polymer (inter)layer;  
'defect free' optical laminate  
comprising a plasticised (meth)acrylate or vinyl ester  
polymer film AND (not necessarily bonded to) a substrate;  
'kit-of-parts' of an amorphous polymer  
film and a NON-VOLATILE, NON-REACTIVE plasticiser for  
forming a laminate with a substrate.

2. Claim : 25

claim 25: 'defect free' laminate comprising a  
plasticised amorphous polymer film and a substrate;

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

|                              |  |
|------------------------------|--|
| International Application No |  |
| PCT/US 99/06016              |  |

| Patent document cited in search report | Publication date | Patent family member(s) |  | Publication date |
|--|------------------|-------------------------|--|------------------|
| US 4358329                             | A 09-11-1982     | NONE                    |  |                  |
| US 4385951                             | A 31-05-1983     | CA 1167362 A            |  | 15-05-1984       |
| US 4341576                             | A 27-07-1982     | AR 228311 A             |  | 15-02-1983       |
|  |                  | AU 531532 B             |  | 25-08-1983       |
|  |                  | AU 8433482 A            |  | 23-12-1982       |
|  |                  | BE 893352 A             |  | 29-11-1982       |
|  |                  | BR 8203162 A            |  | 17-05-1983       |
|  |                  | CA 1155743 A            |  | 25-10-1983       |
|  |                  | DE 3219887 A            |  | 26-05-1983       |
|  |                  | ES 512688 A             |  | 16-04-1983       |
|  |                  | FR 2506670 A            |  | 03-12-1982       |
|  |                  | GB 2099366 A,B          |  | 08-12-1982       |
|  |                  | JP 57209861 A           |  | 23-12-1982       |
|  |                  | NL 8202148 A            |  | 03-01-1983       |
|  |                  | NZ 200636 A             |  | 28-09-1984       |
|  |                  | SE 8203306 A            |  | 02-12-1982       |
|  |                  | ZA 8203502 A            |  | 25-01-1984       |
| US 3449184                             | A 10-06-1969     | NONE                    |  |                  |
| US 4386991                             | A 07-06-1983     | JP 1279500 C            |  | 29-08-1985       |
|  |                  | JP 57117536 A           |  | 22-07-1982       |
|  |                  | JP 60000368 B           |  | 08-01-1985       |
|  |                  | JP 1295295 C            |  | 26-12-1985       |
|  |                  | JP 56115327 A           |  | 10-09-1981       |
|  |                  | JP 60019775 B           |  | 17-05-1985       |
|  |                  | EP 0038115 A            |  | 21-10-1981       |